



INVESTOR IN PEOPLE



The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

**PRIORITY
DOCUMENT**
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

REC'D 27 AUG 2004

WIPO

PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.


I also certify that the application is now proceeding in the name as identified herein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed



Dated

10 August 2004



GB0318027.0

By virtue of a direction given under Section 30 of the Patents Act 1977, the application is proceeding in the name of:-

GTL MICROSYSTEMS AG
Incorporated in Switzerland
Rigistrasse 184
CH-6340, Baar
Switzerland

ADP No. 08754038001



978 55777 705?
02AUG03 EB27048-1 D02834
P01/7700 0-00-0318027.0

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

THE PATENT OFFICE

M

01 AUG 2003

NEWPORT

The Patent Office

Cardiff Road
Newport
South Wales
NP10 8QQ

1. Your reference 15787 MdH

2. Patent application number
(The Patent Office will fill in this part)

0318027.0

= 1 AUG 2003

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Accentus plc
329 Harwell
Didcot
Oxfordshire OX11 0QJ

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

England & Wales

SECTION 30 (1977 ACT) APPLICATION FILED 11/11/03
81258 33001

4. Title of the invention Catalyst structure and catalytic reactor

5. Name of your agent (if you have one)

Peter Turquand MANSFIELD
Accentus plc
Patents Dept
329 Harwell
Didcot
Oxfordshire OX11 0QJ

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Patents ADP number (if you know it)

81322 43001

6. If you are declaring priority from one or more earlier patent applications, give the country

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

Yes

- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
 - c) any named applicant is a corporate body.
- See note (d))

9. Enter the number of sheets for any of the following items you are filing with this form.
Do not count copies of the same document

Continuation sheets of this form

Description

11 ✓

Claim(s)

2 ✓

Abstract

1 ✓

Drawing(s)

1 + 1 ✓

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

1 ✓

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. Peter Turquand MANSFIELD (on behalf of Accentus plc by virtue of a Power of Attorney dated 18th February 2003)

I/We request the grant of a patent on the basis of this application.

Signature

Date 31-7-03

12. Name and daytime telephone number of person to contact in the United Kingdom

Frances Esplin - 01235 432037

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

DUPLICATE

Catalyst Structure and Catalytic Reactor

This invention relates to a process for making a catalyst structure, and to catalytic reactors
5 incorporating that catalyst structure.

A process is described in WO 01/51194 (Accentus plc) in which methane is reacted with steam, to generate carbon monoxide and hydrogen in a first catalytic
10 reactor; the resulting gas mixture is then used to perform Fischer-Tropsch synthesis in a second catalytic reactor. The overall result is to convert methane to hydrocarbons of higher molecular weight, which are usually liquid or solid under ambient conditions. The
15 two stages of the process, steam/methane reforming and Fischer-Tropsch synthesis, require different catalysts, and catalytic reactors are described for each stage. The catalytic reactors enable heat to be transferred to or from the reacting gases, respectively, as the reactions
20 are respectively endothermic and exothermic; the heat required for steam/methane reforming is provided by gas combustion. A known catalyst for the Fischer-Tropsch synthesis utilises small particles of cobalt on a ceramic support which may be produced by dip coating a metal
25 substrate into a slurry of a material from which the ceramic support can be made. A markedly better way of making such a catalyst has now been found.

According to the present invention there is provided
30 a process for coating a metal substrate with a layer of ceramic, the method comprising spraying droplets of a slurry of a ceramic precursor onto a hot metal substrate, the substrate being at a temperature between 650° and 750°C.

35

For example the ceramic layer may be of alumina or

zirconia; to form an alumina layer the slurry may
comprise alumina particles and/or an alumina sol.
Spraying onto a red-hot surface in this fashion leads to
a very marked improvement in adhesion of the resulting
5 ceramic to the metal substrate, so that for example the
substrate can be twisted without the ceramic flaking off.
The spray of droplets must not be so intense as to
significantly cool the metal substrate, and it is
desirable for the droplets to have more than 15% solid
10 material and more preferably about 30%, so that the solid
material sticks to the surface rather than being broken
up by boiling solvent.

Preferably the metal substrate is a steel alloy that
15 forms an adherent surface coating of aluminium oxide when
heated, for example an aluminium-bearing ferritic steel
such as iron with 15% chromium, 4% aluminium, and 0.3%
yttrium (eg Fecralloy (TM)). When this metal is heated
in air it forms an adherent oxide coating of alumina,
20 which protects the alloy against further oxidation and
against corrosion. The substrate may be a wire mesh or a
felt sheet, which may be corrugated or pleated, but the
preferred substrate is a thin metal foil for example of
thickness less than 100 μm .

25 Such a corrugated substrate incorporating catalytic
material may be inserted into a flow channel defined by a
groove in a plate; a catalytic reactor can consist of a
stack of such plates with grooves, the plates being
30 bonded together, and flow channels for the desired
chemical reaction alternating with flow channels to
provide or remove heat. If the desired chemical reaction
is an endothermic reaction such as steam/methane
reforming, then the alternating channels may provide heat
35 by catalytic combustion. On the other hand, if the
desired chemical reaction is an exothermic reaction such

as a Fischer-Tropsch synthesis, then the alternating channels may carry a heat exchange fluid or coolant. The metal substrate of the catalyst structure within the flow channels enhances heat transfer and catalyst surface
5 area.

The metal substrate may be heated in a variety of different ways, but a preferred method is to pass an electrical current through it, so that both sides of the
10 substrate are accessible for spraying. Preferably the droplets are initially in the size range 30 to 150 μm , and they are preferably sprayed using an atomiser using hot gas, the contact with the hot gas promoting evaporation of solvent from the droplets so that the
15 concentration of solid material increases. The spraying process should be carried out in such a way that rapid evaporation of the residual solvent content occurs when the droplets impact with the foil.

20 A desired coating thickness of ceramic can be built up on the substrate by several successive spraying and drying steps, so that for example the final thickness of the ceramic layer may be in the range 30 to 200 μm on each side of the substrate. The ceramic will have
25 mesopores, of characteristic size in the range 2 nm to 20nm, which provide the majority of sites for the dispersed catalyst metal. If the droplets contain only alumina sol, that is to say a material with a primary particle size of about 15 nm which forms a colloidal sol
30 in water, then the resulting ceramic will also have a mainly mesoporous character, subject to any sintering that occurs during calcination. Such a mesoporous ceramic layer would be suitable for a catalyst for reactions such as combustion or reforming. However, for
35 some catalysts such as those for use in Fischer-Tropsch synthesis it is necessary for there to be larger

mesopores and also macropores, that is to say pores of size at least 50 nm and above. Such a macroporous content may be obtained by spraying droplets containing much larger alumina particles, for example gamma alumina
5 with particles of size 15 - 30 μ m, along with some alumina sol to act as a supporting agent and as a binder. The degree of macroporosity can be controlled by changing the proportion of the particulate non-dispersible alumina to alumina sol in the mixture forming the droplets, or by
10 changing the size of the particulate alumina particles. For example, by spraying successive layers with increasing proportions of particulate alumina, a ceramic layer can be formed in which the extent of macroporosity increases towards the outer surface of the layer.

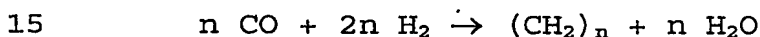
15

The appropriate catalyst for the desired reaction must also be incorporated into the ceramic layer. For example palladium and/or platinum are suitable catalysts for a combustion reaction; rhodium and/or platinum are
20 suitable catalysts for a reforming reaction; and noble-metal promoted cobalt is a suitable catalyst for Fischer-Tropsch synthesis. Such catalyst metals may be deposited in the form of the nitrate salt into the ceramic layer, and then heated and reduced (for example using hydrogen)
25 to the metal. Such an approach can produce catalyst metal in a highly dispersed form consisting of very small crystallites for example of size about 5 nm, which have very high catalytic activity. Where the resulting metal crystallites would react with air, the catalyst structure
30 may be coated with a paraffin wax, which will prevent oxidation during handling.

The invention will now be further and more particularly described, by way of example only, and with
35 reference to the accompanying drawing:

Figure 1 shows a sectional view of a reactor suitable for performing Fischer-Tropsch synthesis, showing a plate in plan.

5 The invention relates to a way of making a catalyst. It particularly relates to a catalyst suitable for Fischer-Tropsch synthesis, which may form part of a process for converting methane to longer chain hydrocarbons. Fischer-Tropsch synthesis is a reaction
10 between carbon monoxide and hydrogen, and this gas mixture may for example be generated by steam/methane reforming. In Fischer-Tropsch synthesis the gases react to generate a longer chain hydrocarbon, that is to say:



which is an exothermic reaction, occurring at an elevated temperature, typically between 200 and 350°C, for example 210°C, and an elevated pressure typically between 2 MPa
20 and 4 MPa, for example 2.1 MPa, in the presence of a catalyst such as iron, cobalt or fused magnetite, with a promoter. The exact nature of the organic compounds formed by the reaction depends on the temperature, the pressure, and the catalyst, as well as the ratio of
25 carbon monoxide to hydrogen.

A preferred catalyst comprises a coating of alumina, with 10-40% (by weight compared to the weight of alumina) of cobalt, and with a ruthenium, platinum and/or
30 gadolinium promoter, the promoter being between 0.01% to 10% of the weight of the cobalt. There may also be a basicity promoter such as ThO₂. The activity and selectivity of the catalyst depends upon the level of dispersion of cobalt metal upon the support, the optimum
35 level of cobalt dispersion being typically in the range 0.1 to 0.2, so that between 10% and 20% of the cobalt

metal atoms present are at a surface. The larger the degree of dispersion, clearly the smaller must be the cobalt metal crystallite size, and this is typically in the range 5-15 nm. Cobalt particles of such a size
5 provide a high level of catalytic activity.

Referring now to figure 1 a reactor 10 for Fischer-Tropsch synthesis comprises a stack of steel plates 12, each plate being generally rectangular, 450 mm long and
10 150 mm wide and 3 mm thick, these dimensions being given only by way of example. On the upper surface of each such plate 12 are rectangular grooves 14 of depth 2 mm separated by lands 15 (eight such grooves being shown), but there are three different arrangements of the grooves
15 14. In the plate 12 shown in the drawing the grooves 14 extend diagonally at an angle of 45° to the longitudinal axis of the plate 12, from top left to bottom right as shown. In a second type of plate 12 the grooves 14a (as indicated by broken lines) follow a mirror image pattern,
20 extending diagonally at 45° from bottom left to top right as shown. In a third type of plate 12 the grooves 14b (as indicated by chain dotted lines) extend parallel to the longitudinal axis.

25 The plates 12 are assembled in a stack, with each of the third type of plate 12 (with the longitudinal grooves 14b) being between a plate with diagonal grooves 14 and a plate with mirror image diagonal grooves 14a, and after assembling many plates 12 the stack is completed with a
30 blank rectangular plate. The plates 12 are compressed together and subjected to a vacuum heat treatment to bring about diffusion bonding, so they are sealed to each other. Corrugated Fecralloy alloy foils 16 (only one is shown) 50 µm thick coated with a ceramic coating
35 containing a catalyst material, of appropriate shapes and with corrugations 2 mm high, can be slid into each such

diagonal groove 14 or 14a.

Header chambers 18 are welded to the stack along each side, each header 18 defining three compartments by virtue of two fins 20 that are also welded to the stack. The fins 20 are one third of the way along the length of the stack from each end, and coincide with a land 15 (or a portion of the plates with no groove) in each plate 12 with diagonal grooves 14 or 14a. Coolant headers 22 in the form of rectangular caps are welded onto the stack at each end, communicating with the longitudinal grooves 14b. In a modification (not shown), in place of each three-compartment header 18 there might instead be three adjacent header chambers, each being a rectangular cap like the headers 22. Within each of the central compartments of the headers 18 there are coolant tubes 25 that extend the entire height of the stack. At the base of each of these central compartments is an outlet duct (not shown) through which liquids condensing onto the tubes 25 can emerge. For use, the reactor 10 is arranged with the plates 12 in substantially horizontal planes so that the coolant tubes 25 are substantially vertical.

In use of the reactor 10 the mixture of carbon monoxide and hydrogen is supplied to the compartments of both headers 18 at one end (the left hand end as shown) of the stack, and so gases produced by Fischer-Tropsch synthesis emerge through the compartments of both headers 18 at the right hand end as shown. The flow path for the mixture supplied to the top-left header compartment (as shown), for example, is through the diagonal grooves 14 into the bottom-middle header compartment, and then to flow through the diagonal grooves 14a in other plates in the stack into the top-right header compartment. A coolant is supplied to the header 22 at the same end of the stack, to maintain the temperature within the reactor

10 at about 210°C, so that the coolant is at its lowest temperature at the area where heat generation is at its maximum during the first stage. Hence the flows of the reacting gases and the coolant are at least partially co-
5 current. The intention is to approach isothermal conditions throughout the reactor 10; this has the advantage of minimising the risk of any wax (i.e. very long chain hydrocarbon) blocking the flow channels towards the outlet from the reaction channels. The flow
10 rate (space velocity) of the reacting gases is in the range 1000 - 15000 /hr, so as to ensure that the conversion of carbon monoxide is only about 60% by the time the gases reach the middle compartments of the headers 18, so that the water vapour does not exceed 20
15 mole% (and its partial pressure does not exceed 0.4 MPa).

The coolant tubes 25 are supplied with coolant at a different temperature so that they are at a lower temperature, for example at 150°C (which is below the
20 boiling point of water at the pressure in the reactor). Consequently water vapour (and some of the longer-chain hydrocarbons) condenses on the outer surface of the coolant tubes 25, and runs down those tubes 25 to emerge from the outlet duct (not shown) at the bottom of the
25 stack. This significantly reduces the partial pressure of water vapour in the gas mixture that flows on into the next set of diagonal grooves 14 or 14a. The result is that the Fischer-Tropsch synthesis takes place in two successive stages - the first stage being as the gas
30 flows from the inlet compartments of the headers 18 to the middle compartments; and the second stage being as the gas flows from the middle compartments to the outlet compartments - and at least part of the water vapour generated in the first stage is removed from the gas
35 stream before it enters the second stage.

The catalyst-carrying foils 16 are produced as follows. A colloidal sol is made by combining water-dispersible alumina with water, the alumina having a primary particle size of about 15 nm that form
5 agglomerates of size about 110 nm; the specific surface area may be in the range 140 - 350 m²/g. The pH of the sol is adjusted with ammonium hydroxide to lie in the range pH 8.5 - 9.5. This sol is mixed with gamma alumina stabilised with 3% lanthanum oxide, this non-dispersible
10 alumina having a mean particle size about 30 μ m, with pores of size 5-20 nm, and a specific surface area in the range 140 - 350 m²/g. The proportions are preferably such that the sol alumina is between 3 and 10% by weight of the resulting mixture, more preferably between 3 and 5%,
15 and that the particulate alumina is between 12 and 35% by weight of the resulting mixture. For examples the sol alumina may be 3% and the particulate alumina 27% by weight of the mixture (so that the sol alumina is 10% of the total alumina). This mixture is thoroughly blended
20 to form a suspension.

A corrugated Fecralloy foil is heated electrically to 700°C, and is held at this temperature, and the suspension of alumina is sprayed onto the foil using an
25 atomiser using hot air, the droplets typically having a mean size in the range 30 μ m to 150 μ m. Contact with the hot gas promotes some evaporation of the water so that the droplets that reach the surface of the foil have a somewhat greater proportion of solids. Rapid evaporation
30 of residual water occurs as the droplets impact with the foil, and a strong bond is formed between the alumina from the droplets and the oxide on the surface of the foil. This rapid evaporation ensures that there is no tendency for the suspension to flow over the surface to
35 form pools in the bottoms of corrugations. The ceramic layer is built up by several successive spraying steps,

to achieve a thickness typically between 50 and 200 μm ,
for example 100 μm , on each side of the foil.
Substantial uniformity of the thickness is ensured by
changing the arc of the spray head so that all the
5 surfaces receive a similar mass of droplets.

It will be appreciated that the way in which the
droplets are formed is not critical to the invention, and
that they might alternatively be made by other processes,
10 such as ultrasonic spraying or electrostatic spraying.
It will also be understood that the particulate alumina
might have a different mean particle size, say between
say 5 μm and 40 μm , more preferably in the range 15 μm to
30 μm .

15

Preferably the ceramic layer has a macropore volume
of 0.5 ml/g, for Fischer-Tropsch catalysis. It is also
desirable for the macroporosity to be greater nearer the
exposed surface to facilitate egress of liquid product.
20 This can be achieved by making alumina suspensions
containing different proportions of dispersible (sol) and
non-dispersible (particulate) alumina. For example the
first sprayed suspension might contain 4% (by weight) sol
alumina and 12% particulate alumina; the next suspension
25 might contain 3% sol alumina and 12% particulate alumina;
the next suspension 3% sol alumina and 17% particulate
alumina; and a final suspension of 3% sol alumina and 27%
particulate alumina. The proportion of sol alumina
(which acts as a binder) would thus progressively
30 decrease from 25% to 10% in the successively sprayed
suspensions, but in each case alumina forms at least 15%
by weight of the suspension.

The ceramic layer is then calcined using a slow
35 temperature ramp (eg. 1°C/min) up to 550°C and held for 4

hours, before being cooled. It is then sprayed with hydrated cobalt nitrate dissolved in acetone (which has a low surface tension and a low viscosity), or in a mixture of acetone and water, and then heat treated and reduced at elevated temperature in the presence of hydrogen. The promoter may be impregnated along with the cobalt. The reduction forms cobalt metal crystallites in the range 5-15 nm, which provide a high level of catalytic activity. The surface is then coated with paraffin wax and to protect it from air. The corrugated foil with the catalyst coating can then be inserted into the reactor as described in relation to figure 1. Heating the reactor to its operating temperature melts the wax, which is then carried out of the reactor by the gas flows.

Although the method has been described in the context of making a Fischer-Tropsch catalyst, it will be appreciated that it may be used for other catalysts. It is particularly beneficial where significant macroporosity or graded porosity is required.

Claims

1. A process for coating a metal substrate with a layer of ceramic, the method comprising spraying droplets of a
5 slurry of a ceramic precursor onto a hot metal substrate, the substrate being at a temperature between 650° and 750°C.
2. A process as claimed in claim 1 wherein the droplets
10 comprise at least 15% solid material.
3. A process as claimed in claim 1 or claim 2 wherein the metal substrate comprises an aluminium-bearing ferritic steel.
15
4. A process as claimed in any one of the preceding claims wherein the substrate is heated electrically.
5. A process as claimed in any one of the preceding
20 claims wherein the droplets are initially in the size range 30 to 150 μm .
6. A process as claimed in any one of the preceding claims wherein the droplets are formed with an atomiser
25 using hot gas.
7. A process as claimed in any one of the preceding claims wherein the layer is built up by successively spraying droplets of slurries of different compositions.
30
8. A process as claimed in claim 7 wherein the compositions are such that the layer increases in macroporosity towards its exposed surface.
- 35 9. A process of making a catalyst, comprising coating a metal substrate with a layer of ceramic by a process as

claimed in any one of the preceding claims, and
incorporating catalyst material into the ceramic layer.

10. A process as claimed in claim 9 wherein the catalyst
5 material is a catalytic metal, and the catalytic metal is
incorporated by contacting the ceramic layer with a
solution of a salt of the metal in a solvent comprising
an organic liquid whose surface tension and viscosity are
lower than those of water.

10

11. A process as claimed in claim 9 or claim 10 wherein
the ceramic layer incorporates a catalytic metal, and is
then coated with wax to protect it from the atmosphere.

15 12. A catalyst made by a process as claimed in any one
of claims 9 to 11.

13. A catalytic reactor incorporating a catalyst as
claimed in claim 12.

20

14. A method of coating a metal substrate substantially
as hereinbefore described.

25 15787 MdH

P T Mansfield
Chartered Patent Agent
Agent for the Applicant

Abstract

Catalyst Structure and Catalytic Reactor

5 A metal substrate is coated with a layer of ceramic,
by spraying droplets of a slurry of a ceramic precursor
onto the substrate, the substrate being at a temperature
between 650° and 750°C. The ceramic may be of alumina,
and may be made macroporous by spraying a mixture of
10 alumina sol and alumina particles. Spraying onto a red
hot surface in this fashion leads to a very marked
improvement in adhesion of the resulting ceramic to the
metal substrate. A catalytically active material may
then be incorporated in the ceramic layer, so as to form
15 a catalyst structure (16).

15787 MdH

Fig.1.

